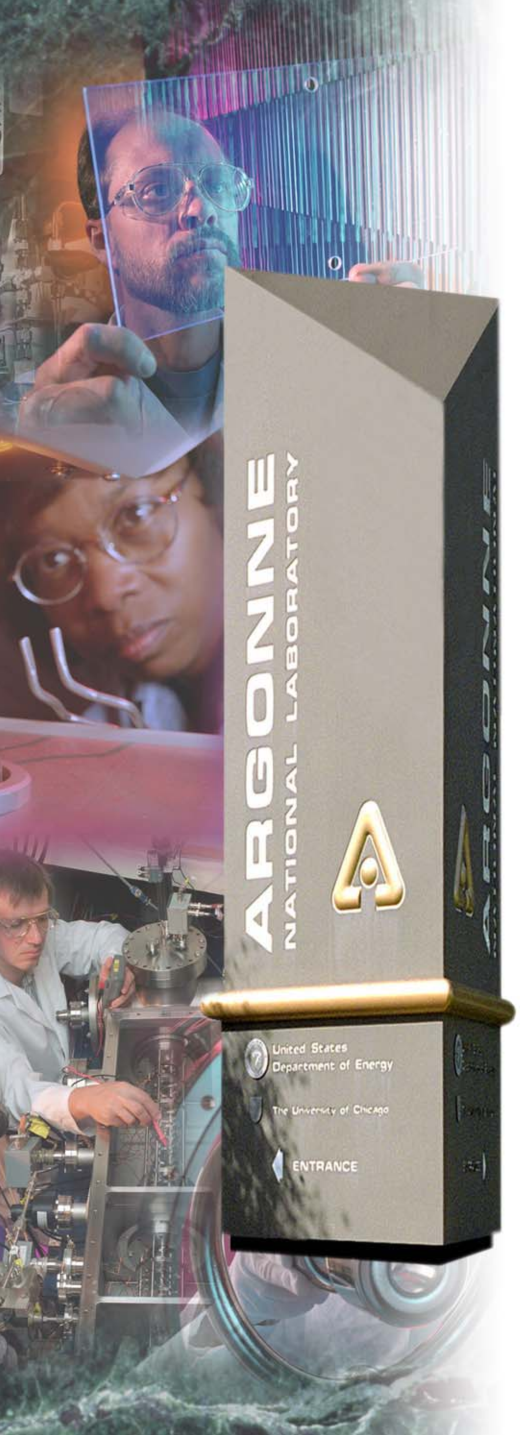


Theoretical Modeling of Nanoscale Confined Light: From Metal Nanoparticles to Nanoholes

Stephen K. Gray
Chemistry Division and
Center for Nanoscale Materials

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Collaborators

Argonne Experimental Groups:

G. Wiederrecht and coworkers,

L. Yin, U. Welp, V. Vlasko-Vlasov and coworkers

Theorists:

S.-H. Chang (Argonne/Northwestern),

T.-W. Lee (Argonne),

and G. C. Schatz (Northwestern)

Supported by: Office of Basic Energy Sciences,
US Department of Energy

Outline

- Motivation
- Methods
- Results :
  - Isolated Ag Nanowires
  - Nanowire Arrays
  - TIR Excitation
  - Isolated Holes

- Concluding Remarks

Motivation

The nature of light interaction with metal nanoparticle (MNP) or nanohole systems could lead to:

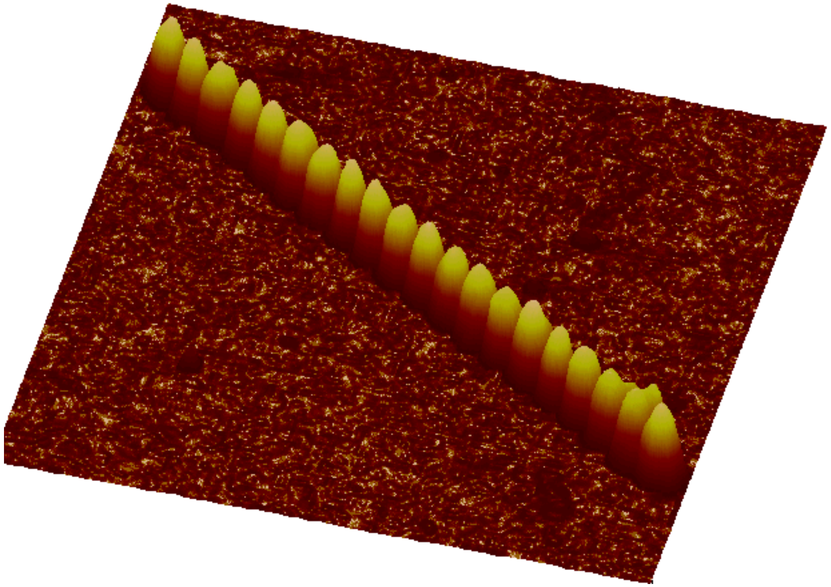
- Nanoscale optical/opto-electronic devices

- Novel chemical and biological sensors

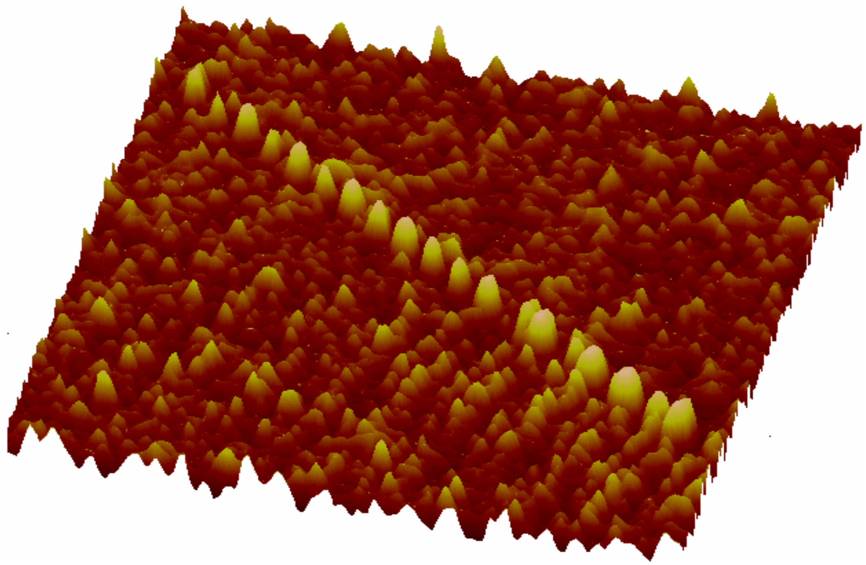
Lots of interesting experiments are being carried out throughout the world -- theory and computation are needed!

Chain of Ag Nanoparticles

Wiederrecht and co-workers (ANL): AFM (topography) and NSOM (near field strengths) on Ag particle arrays

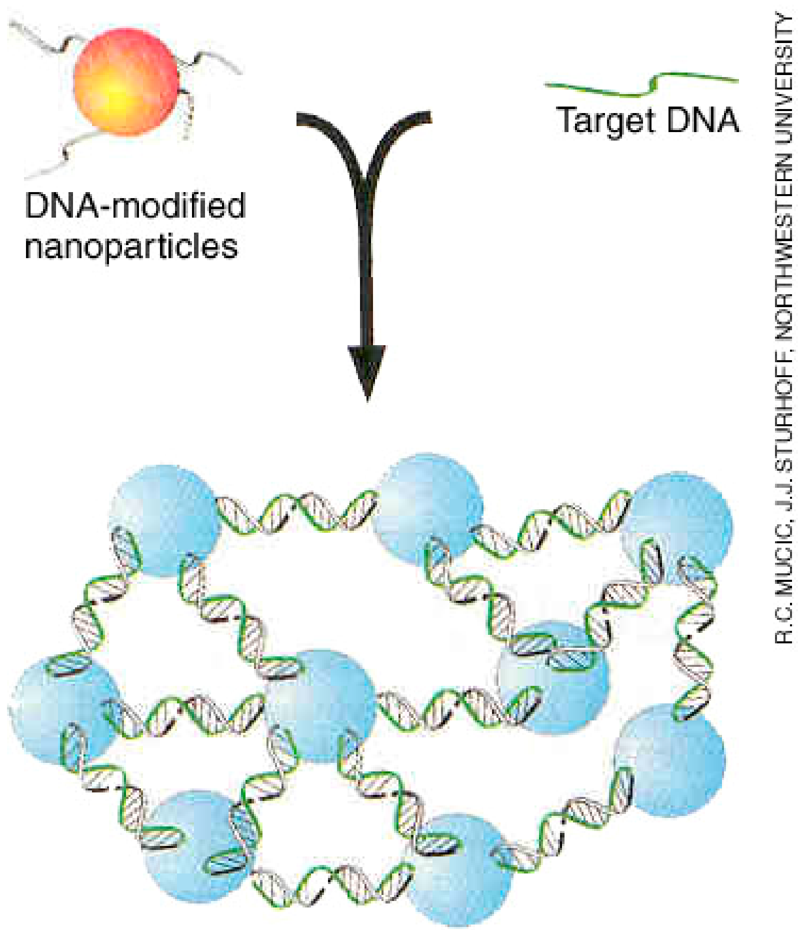


AFM



NSOM

size ~ 100 nm width, periodicity ~ 200 nm



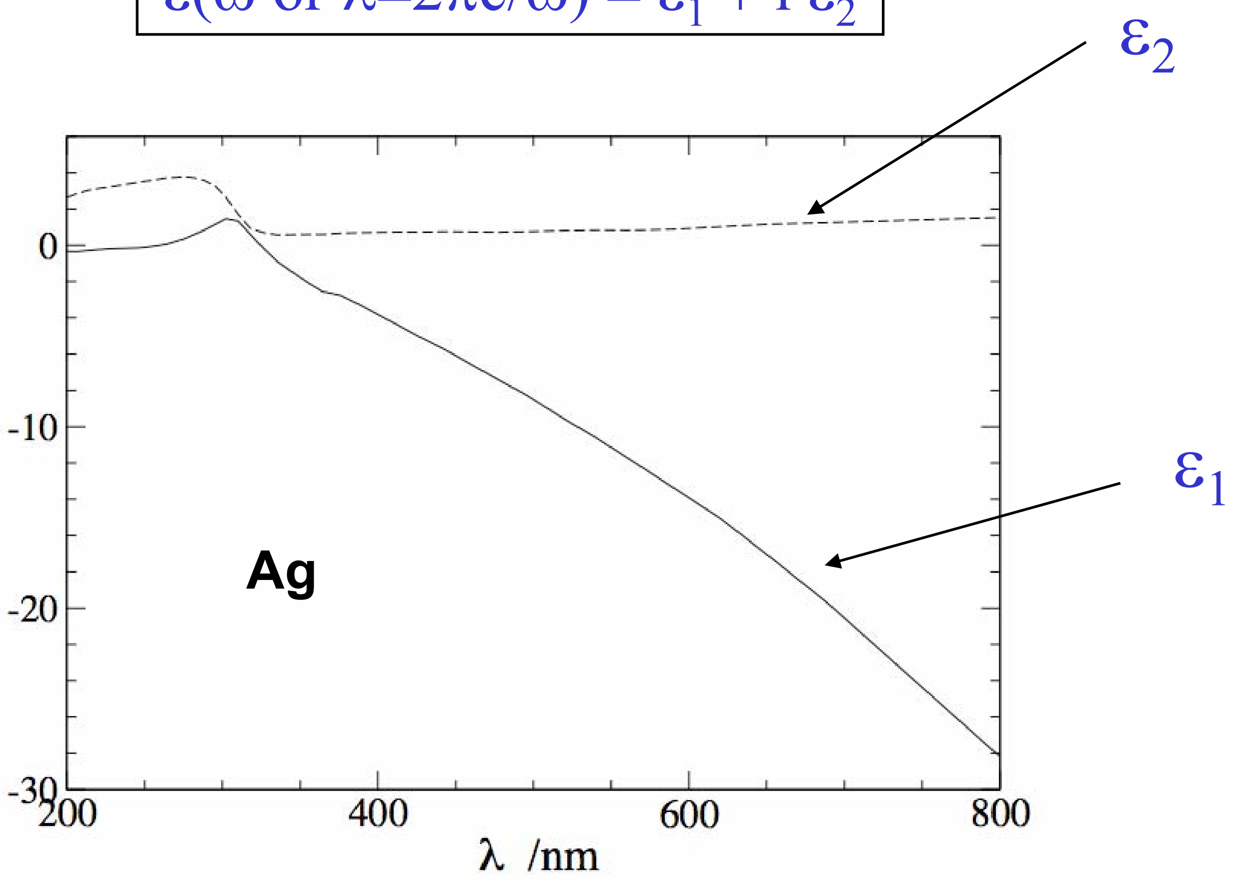
Hybrid web. DNA strands on nanoparticles seek out target DNA, forming a network.

Most potential applications aim to tap the properties of surface plasmons (SPs) -- resonant interactions of light with (induced) charge density in the MNP surface.

E.g., in Mirkin's biological sensors, the SP resonance scattering blue-shifts when Au MNPs bind to DNA in manner shown.

Origins of Surface Plasmons: Re[ε] < 0 in Metals

$$\varepsilon(\omega \text{ or } \lambda=2\pi c/\omega) = \varepsilon_1 + i\,\varepsilon_2$$



Standard heuristic argument

E.o.m. for electron (in a metal) displacement in an electric field:

$$m\ddot{x} + (m/\tau)\,\dot{x} = -q\,E_x\,e^{-i\omega t}$$

Assume $x(t) = x_o\,e^{-i\omega t}$ to get

$$x_o = (q\,E_x/m)/(\omega^2 + i\omega/\tau)$$

Polarization for number density *n:*

$$P_x = n\,(-q x_o) = \chi\,\varepsilon_o\,E_x$$

$$= (\varepsilon - 1)\,\varepsilon_o\,E_x$$

Solve for relative dielectric constant, ε:

$$\boxed{\varepsilon(\omega) = 1 - \omega_p^2/(\omega^2 + i\omega/\tau)}$$

$$\omega_p = \sqrt{nq^2/m\varepsilon_o}$$

Drude model

Surface Plasmons

For Re[ε] < 0, strong oscillations in electric charge are predicted which allow for electromagnetic surface waves, which can have longitudinal components but decay rapidly away from a surface ("evanescent")

Local Surface Plasmons (LSP's) : Confined to nanoparticle surfaces or nanohole inner surfaces; akin to bound (or resonance) states in QM.

Surface Plasmon Polaritons (SPP's) : Confined to metal surfaces but traveling surface plasmons. Typically generated on flat thin metal films.

Methods

"Real theory", if possible, is best but for exploring somewhat complicated nanophotonics systems robust, reasonably accurate and easy to use computational methods are also helpful.

Finite-Difference Time-Domain (FDTD) Method

Basic idea and numerical method is somewhat old :

K. S. Yee, IEEE Trans. Antennas and Propagation, **14**, 302 (1966).

Modern implementations are discussed in :

A Taflove and S. C. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method*, 2nd Ed., (Artech House, Boston, 2000).

- Solve t-dependent form of Maxwell's equations: discretizing in both space and time to generate $\mathbf{E}(\mathbf{x}, t)$ and $\mathbf{H}(\mathbf{x}, t)$ via straightforward time-stepping.

- Staggered grids used for more accurate finite differences and preservation of certain symmetries.

- Current fields are introduced to describe the metallic dielectric constant behavior which can have $\mathrm{Re}[\varepsilon(\omega)] < 0$.

Maxwell's Equations

<u>Outside</u> each nanoparticle:

$$\partial \mathbf{E}(\mathbf{x},t)/\partial t = \nabla \times \mathbf{H}(\mathbf{x},t)/\varepsilon(\mathbf{x})$$

$$\partial \mathbf{H}(\mathbf{x},t)/\partial t = -\nabla \times \mathbf{E}(\mathbf{x},t)/\mu_o$$

<u>Inside</u> each nanoparticle region:

$$\partial \mathbf{E}(\mathbf{x},t)/\partial t = [\nabla \times \mathbf{H}(\mathbf{x},t) - \mathbf{J}(\mathbf{x},t)]/\varepsilon_\infty$$

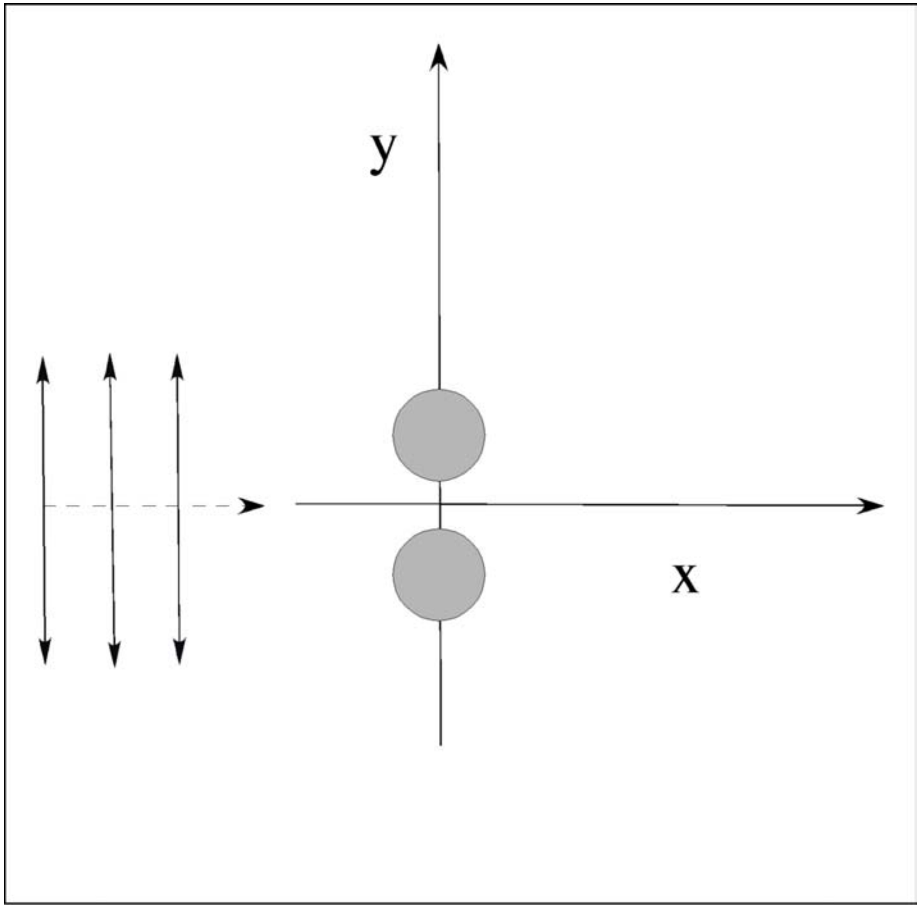
$$\partial \mathbf{H}(\mathbf{x},t)/\partial t = -\nabla \times \mathbf{E}(\mathbf{x},t)/\mu_o$$

$$\partial \mathbf{J}(\mathbf{x},t)/\partial t = \varepsilon_o \omega_p^2\, \mathbf{E}(\mathbf{x},t)/\mu_o - \nu \mathbf{J}(\mathbf{x},t)$$

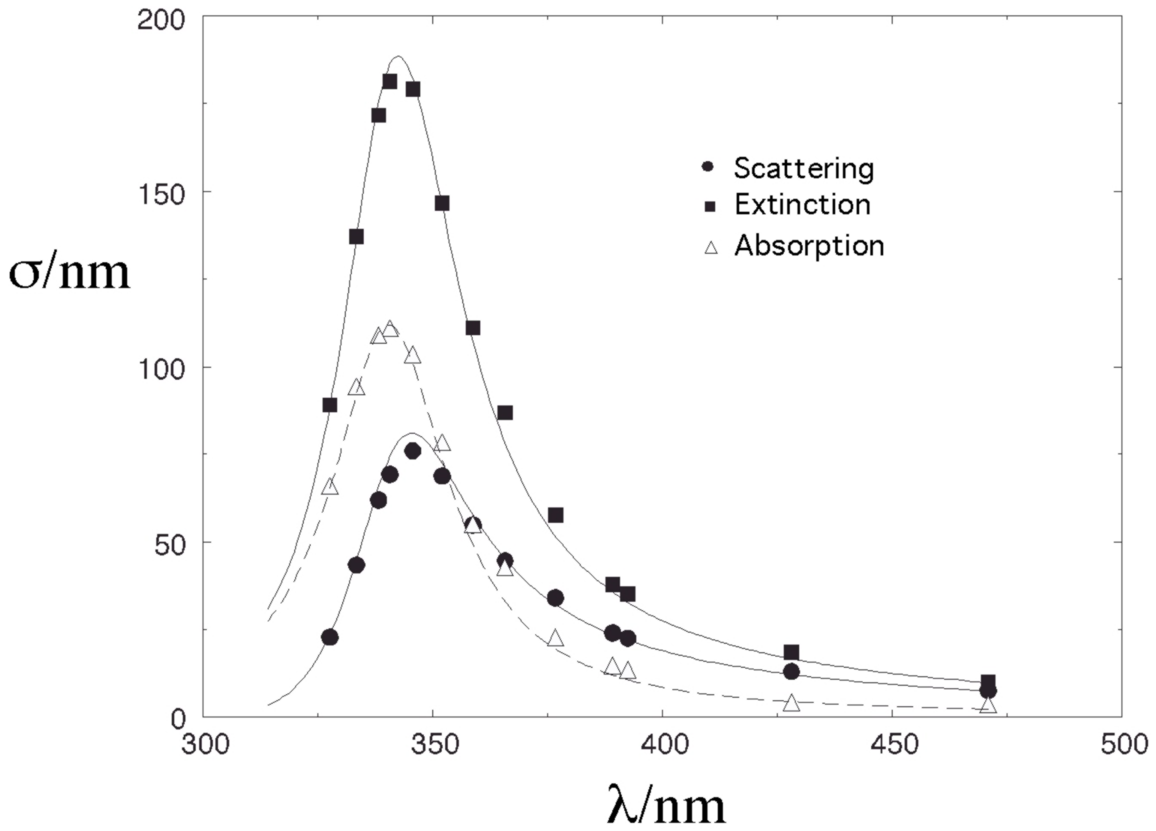
(Parameters for current terms chosen to fit metal dielectric constant data in some frequency range)

Metal Nanowires

Nanoscale cross sections with infinite extension out of (x,y) plane:



FDTD approach is reasonably quantitative even for frequency (or wavelength) resolved scattering



Single Ag cylinder, radius 25 nm :

SP resonance at 350 nm

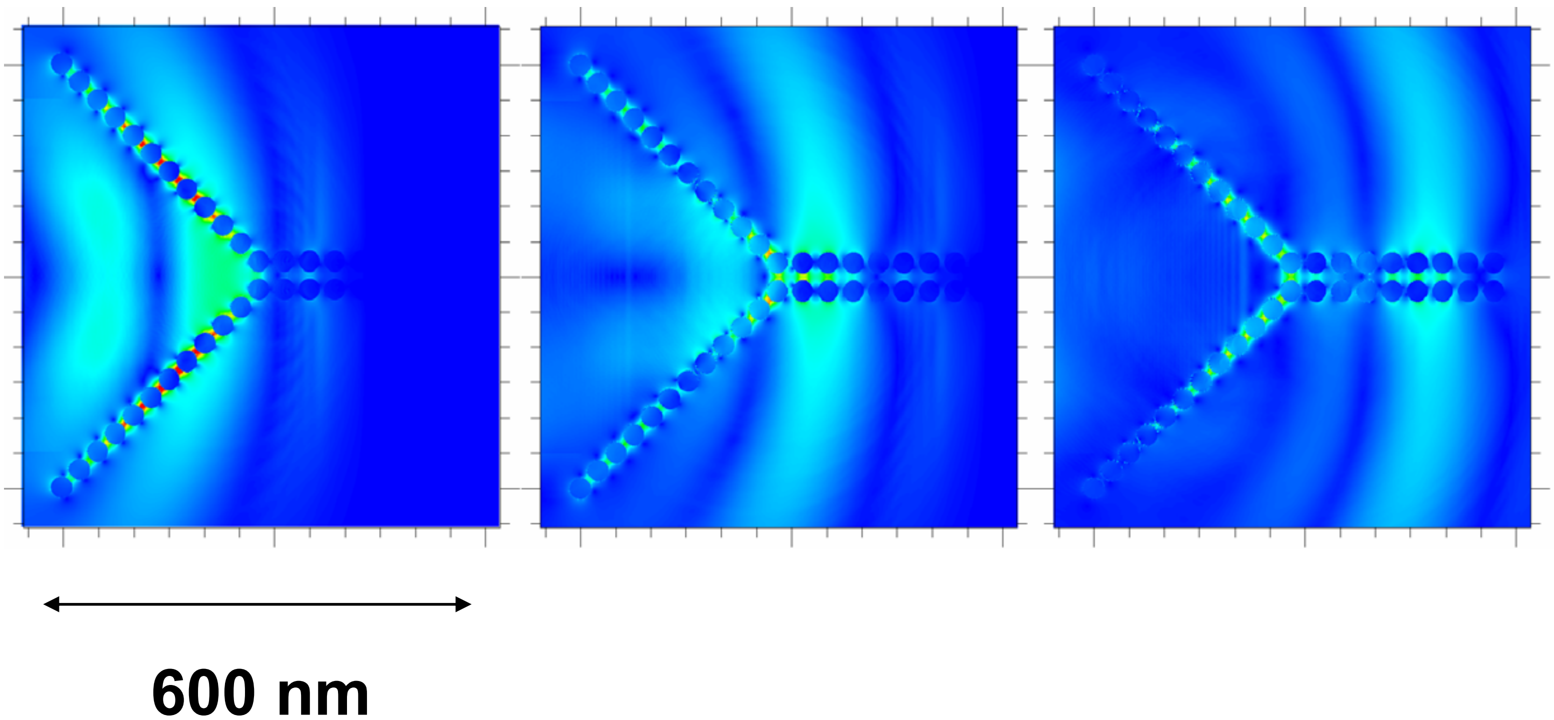
Symbols: FDTD result based on Fourier transforms of numerically generated, time-dependent fields

Curves: Analytical results ("Mie theory").

Funnel Configuration of Ag Nanowires

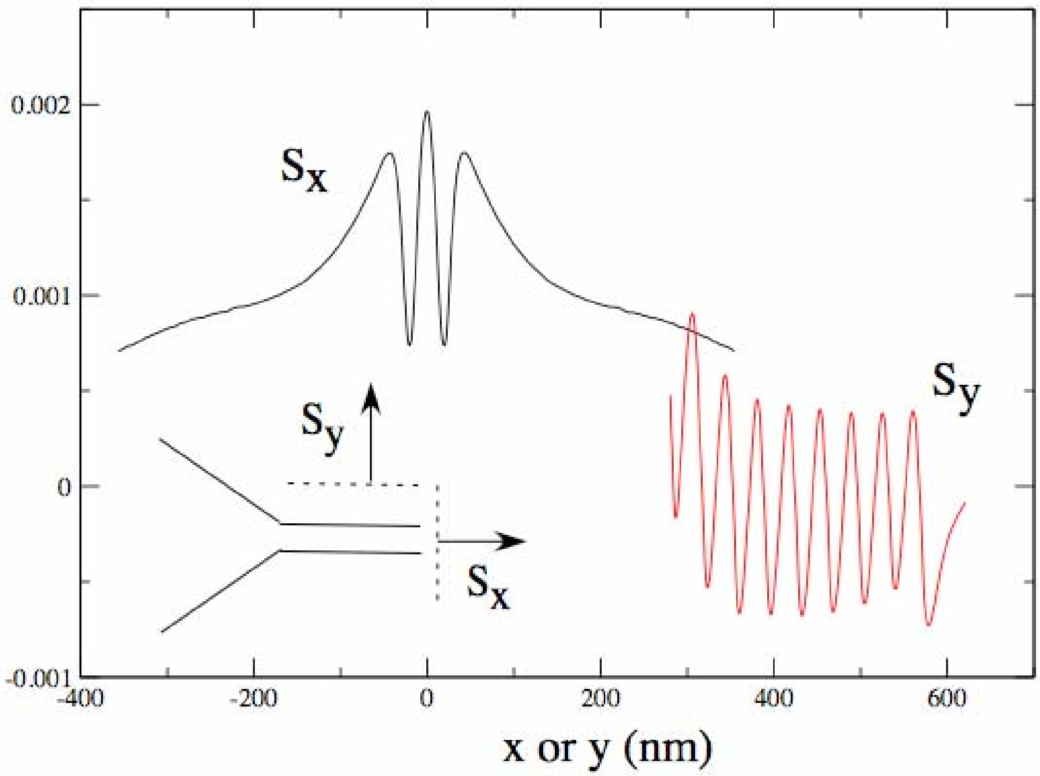
[Gray and Kupka, Phys. Rev. B **68**, 045415 (2003)]

E field at 0.5 fs time intervals:



Can achieve 100 nm nanoscale localization of light.

Time-averaged Flux

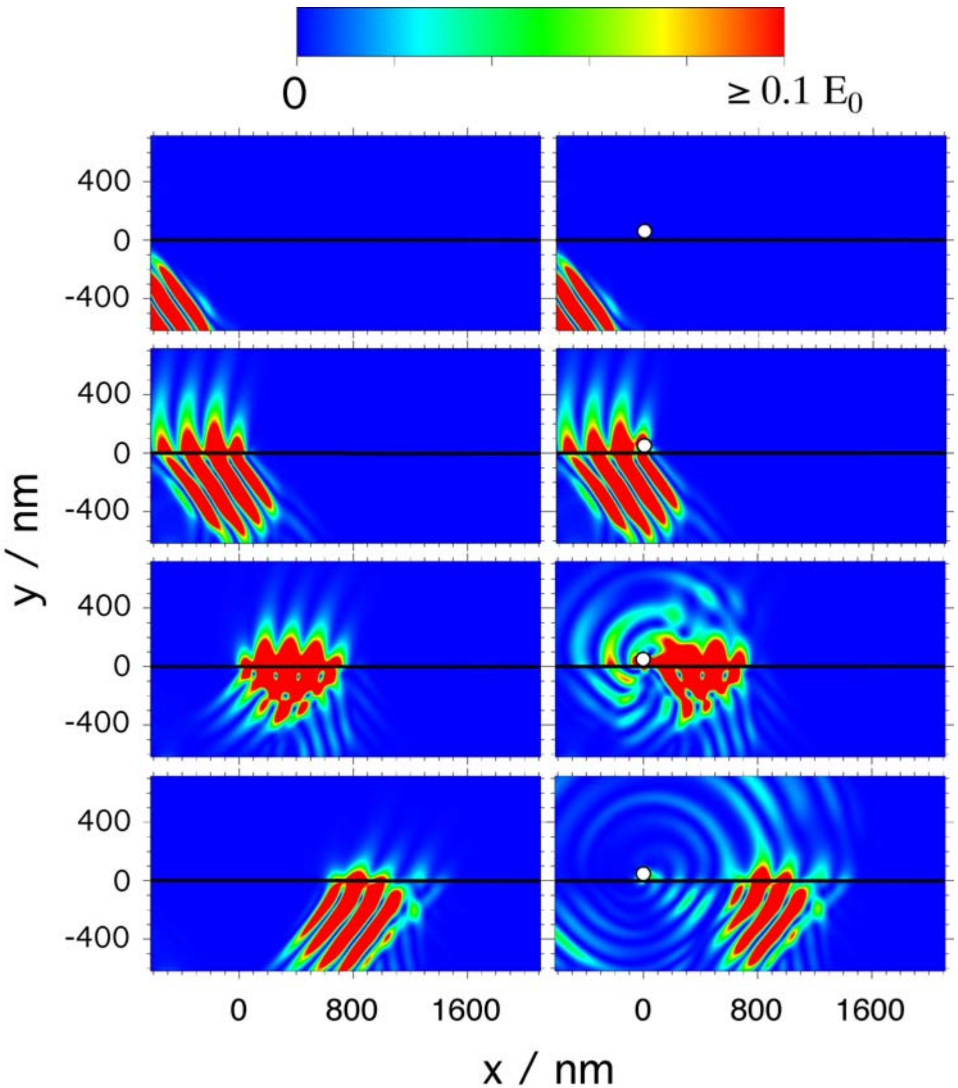


Evanescent Excitation and Scattering of Ag Nanowires

- Wurtz, Im, and Wiederrecht: find metal nanoparticles, scatter light at small angles above dielectric/air interface in "Total Internal Reflection" experiments.

- Calculations have begun to explore this process.

TIR Excitation with FDTD [Wurtz et al., J. Phys. Chem. B. **51**, 14191 (2003)]



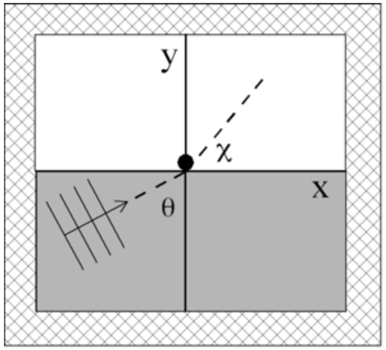
Left panels, top to bottom, show TIR in absence of nanowire.

Right panels, top to bottom, show what happens with a 50 nm radius Ag cylinder.

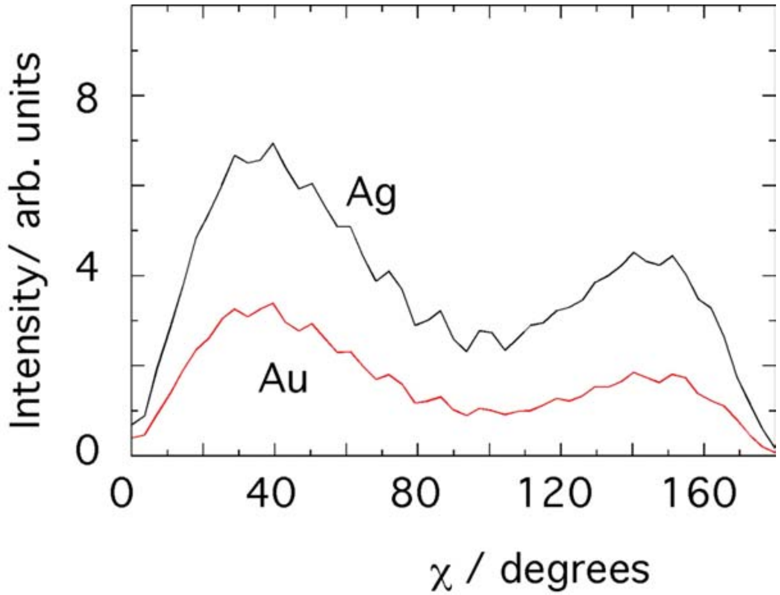
Glass (n=1.5) for y < 0, air (n=1) for y ≥ 0.

Low angle scattering

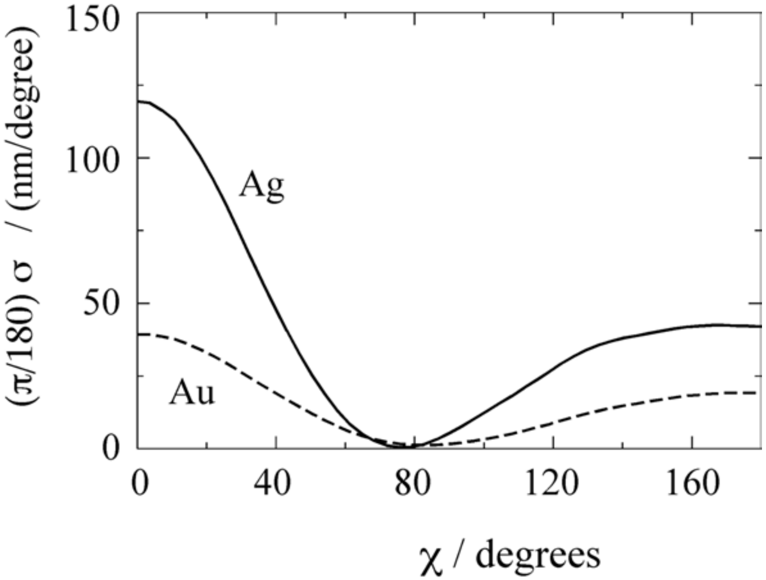
Incident light closer to Ag SP resonance than the Au one.



1 particle/surface



1 particle, free space



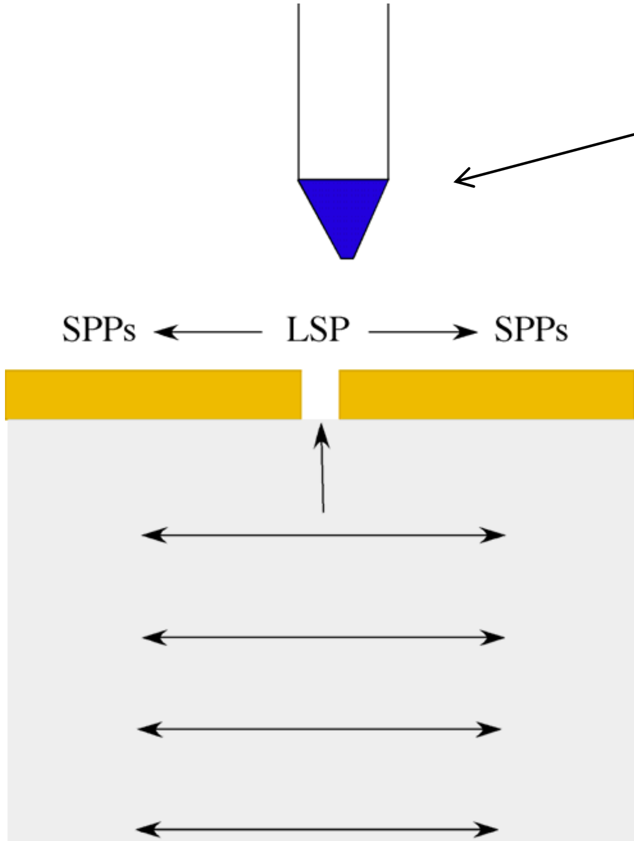
Nanoholes in Thin Metal Films (S.-H. Chang)

- Metal films with nanoscale holes are also of interest -- local SPs similar to those in metal nanoparticles can be excited on hole edges. Furthermore, coupling to SPP's can also occur.

- L. Yin, U. Welp, V. Vlasko-Vlasov and coworkers are exploring such nanoholes at Argonne.

The Type of Experiment :

Scanning near field probe

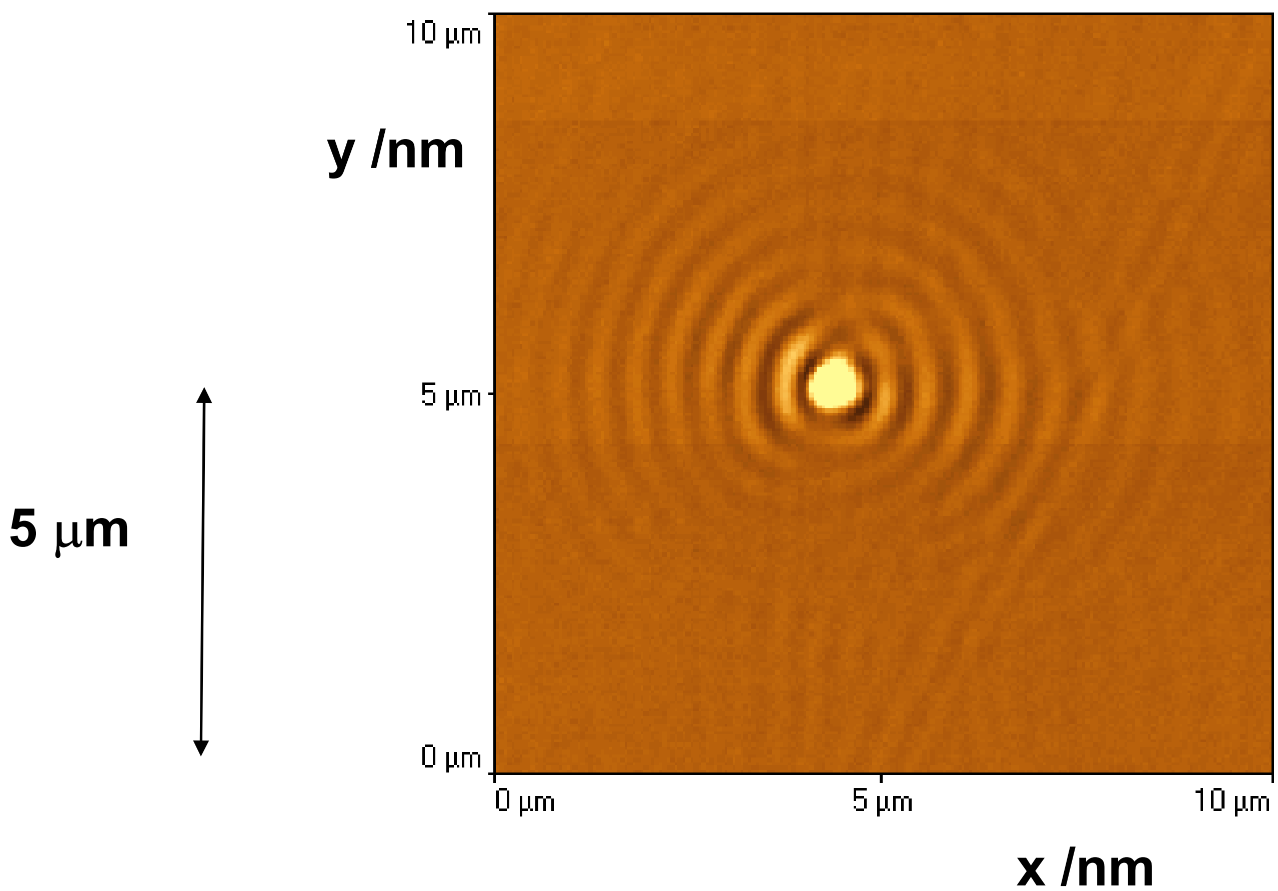


Metal film (e.g., Au or Ag) with holes

Glass substrate with laser light propagating up to metal film

Experimental Results: λ Fringes

170 nm diameter hole in a 100 nm thick Au film on glass. 530 nm light. A view from the air-Au top: ≈ 470-480 nm fringes



x-polarized light

$$\lambda_{SPP} = \sqrt{\frac{\varepsilon_M + 1}{\varepsilon_M}}\,\lambda_{inc} = \sqrt{\frac{-4.67+1}{-4.67}}\ 532\ nm \approx 472\ nm$$

But SPPs alone cannot be seen easily:

$$\boxed{E_x \approx C\ \exp(ik_{SPP}x) \Rightarrow I = E_x E_x^* \approx C^2}$$

Suppose instead:

$$\boxed{E_x \approx C\ \exp(ik_{SPP}x) + A\ \exp(iS)}$$

Then:

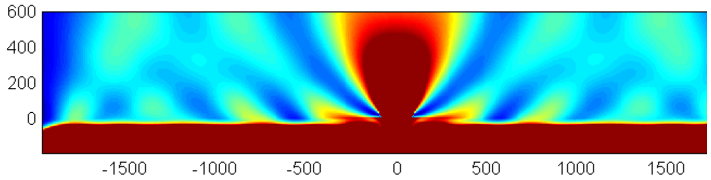
$$\boxed{I = E_x E_x^* \approx C^2 + A^2 + 2CA\ \cos(\ k_{SPP}x + S\ )}$$

$$\boxed{k_{SPP} = 2\pi / \lambda_{SPP} \Rightarrow \lambda_{SPP}\ \ fringes}$$

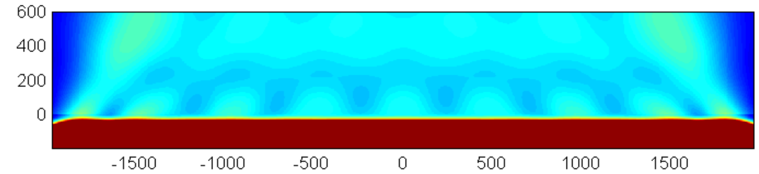
But what is A exp(iS) ?

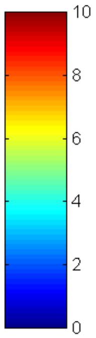
A exp(iS) = T = a Directly Transmitted Wave

$|\text{Hole/Film}|^2$

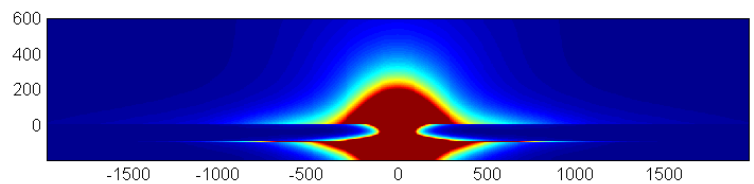


$|\text{Film}|^2$





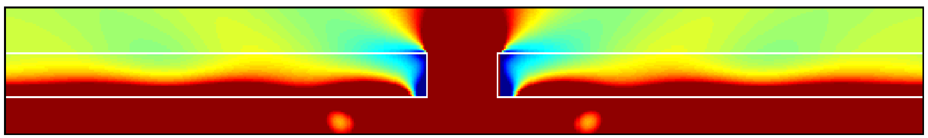
$|\text{ Hole/Film - Pure Film}|^2$



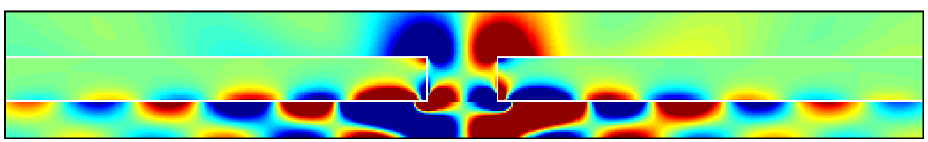
1 μm

Poynting Vector

Flux upwards



Flux sideways



0.3 μm

2 μm

Nanoholes act as "Point Sources" of SPP's

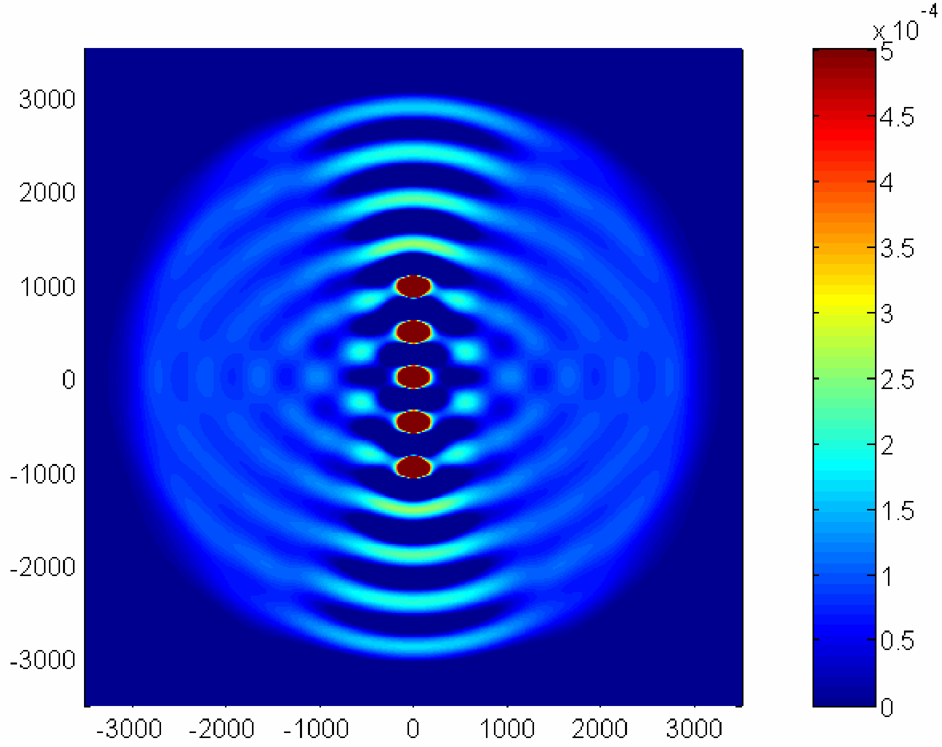
- Near the top plane of the metal surface, we find:

$$\boxed{E_x(r,\varphi,z) \;\propto\; C\,\frac{\exp(\,ik_{SPP}\;r - \;\gamma\;z\,)}{\sqrt{\,r}}\cos(\varphi) \;+\; T_x}$$

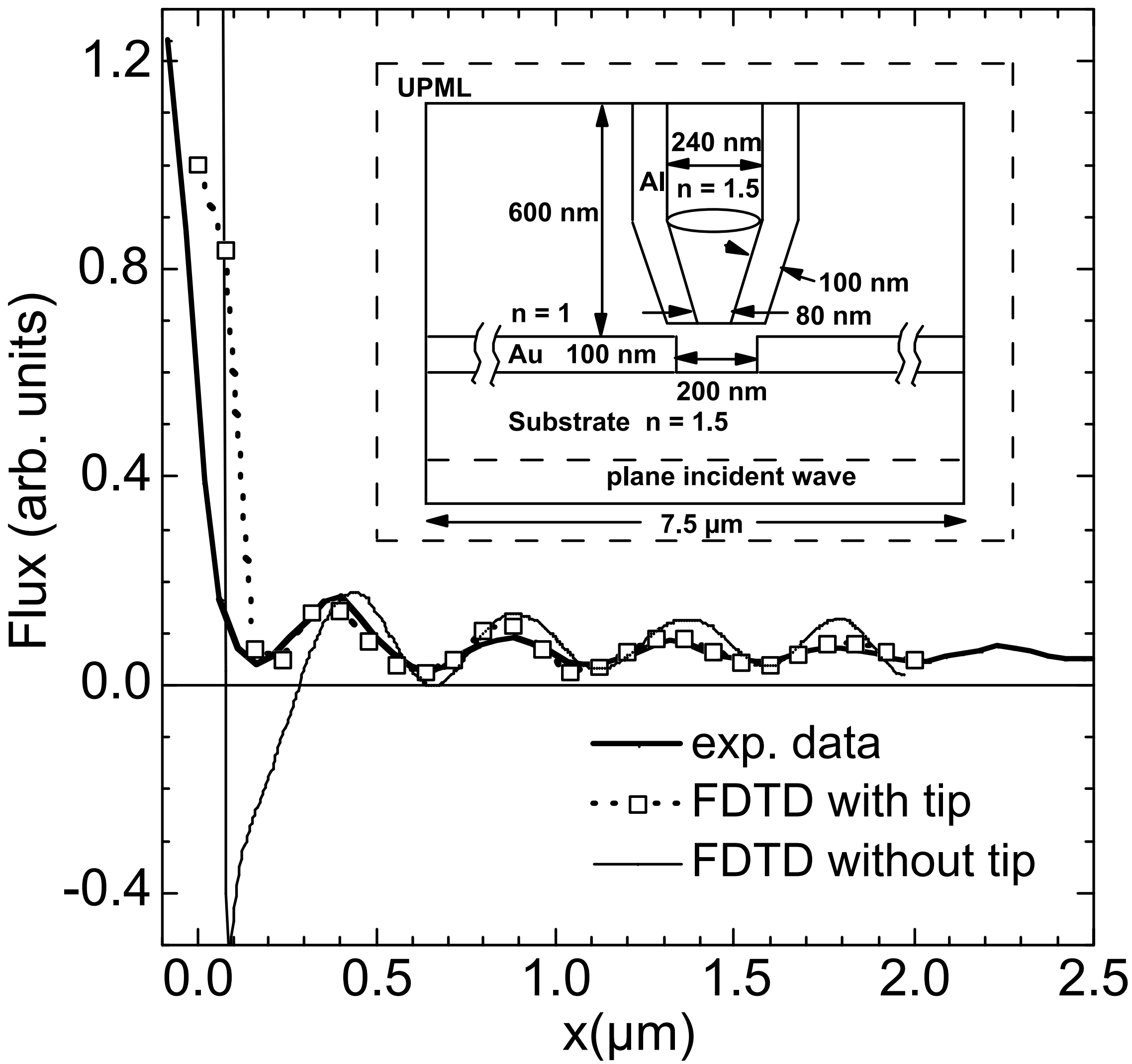
where x-polarized [cos(φ)] light is assumed.

- Despite fact λ_{inc}, λ_{SPP} > 3 d_{hole}, a limited kind of "Huygen's principle" appears to apply to planar SPP's …

Nanohole Arrays for Stronger SPP Beams



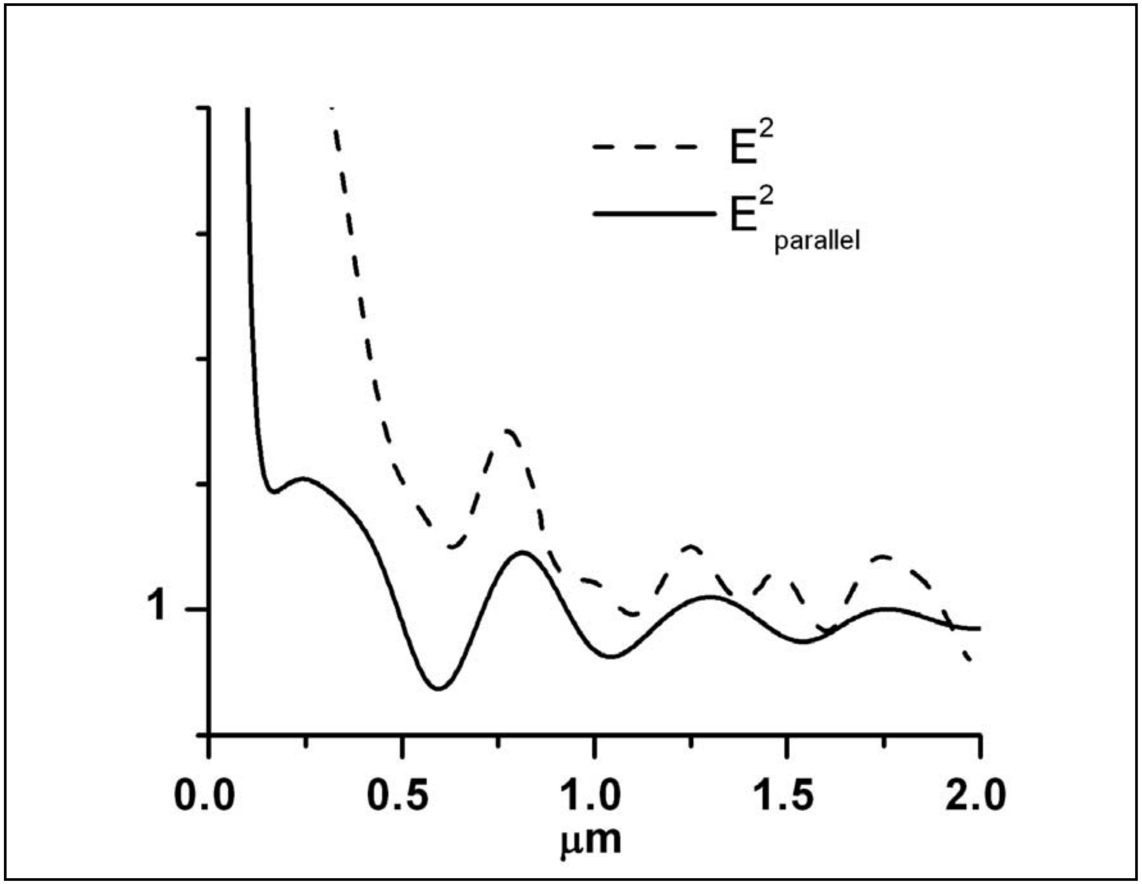
Can also explicitly model the NSOM probe



Yin et al., *Appl. Phys. Lett.* **85**, 467 (2004).

Probe develops dipolar oscillation with incident (x) polarization, interacts with/picks up information about $|E_x|^2$ (not $|E_{tot}|^2$).

Parallel (x) component shows more clear fringes



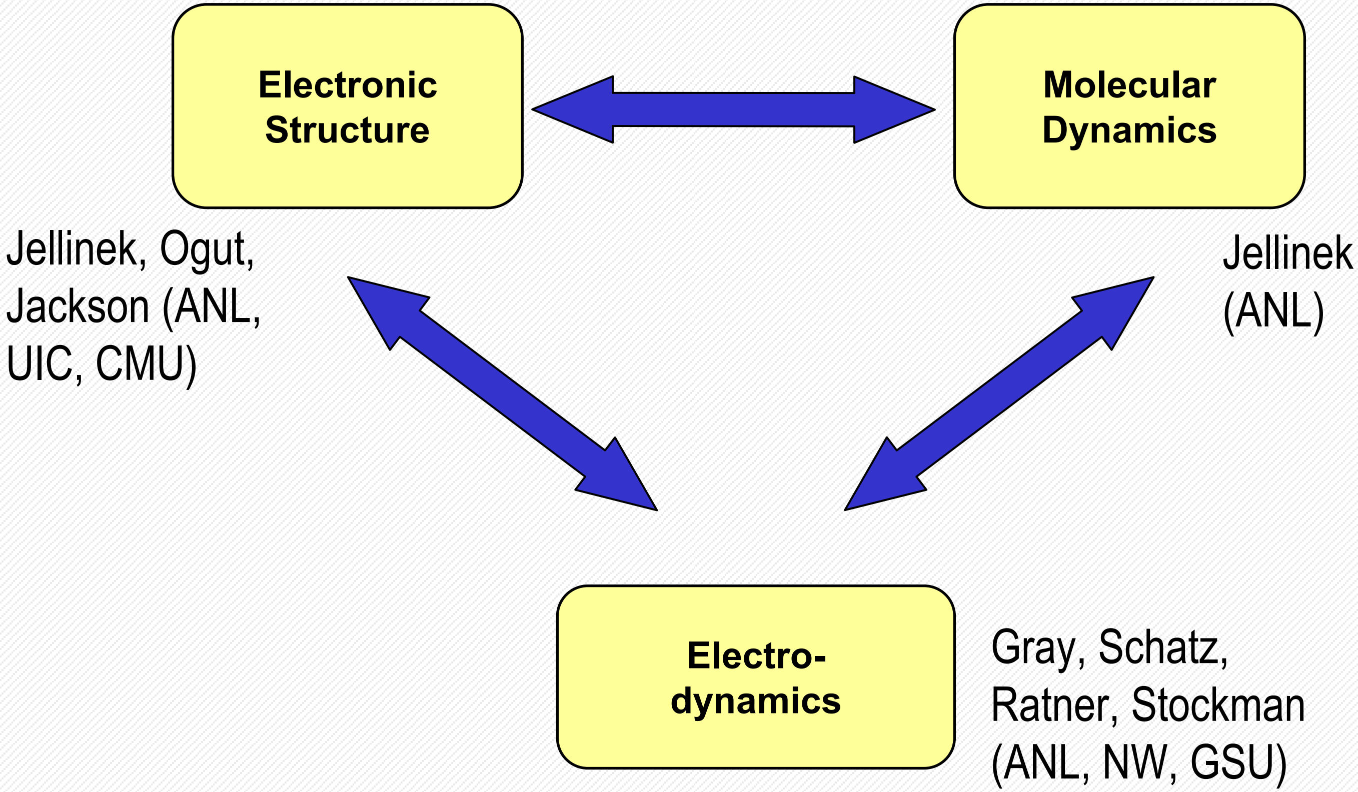
Concluding Remarks

- Demonstrated FDTD approach can yield optical cross sections for metallic nanowire problems.
- Arrays of nanowires investigated: funnel configurations show 100 nm scale localization of light.
- Total Internal Reflection (TIR) excitation/scattering by nanoparticle systems investigated.
- Nanoholes investigated -- demonstrated how SPP’s reveal themselves through interference.

Future Directions

- Multiscale Modeling of Nanophotonics
- Coherent Control of Nanophotonics
- "Killer Apps" ??

Multiscale Approach to Modeling Nanophotonics Problems:



Applied Math/High-Performance Component Infrastructure

Fischer, Norris, Smith (ANL)